

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C08F 8/28, D21H 17/38	A1	(11) International Publication Number: WO 00/11046 (43) International Publication Date: 2 March 2000 (02.03.00)
(21) International Application Number: PCT/US99/18706		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
(22) International Filing Date: 13 August 1999 (13.08.99)		
(30) Priority Data: 09/136,855 19 August 1998 (19.08.98) US		
(71) Applicant: HERCULES INCORPORATED [US/US]; Hercules Plaza, 1313 North Market Street, Wilmington, DE 19894-0001 (US).		
(72) Inventors: GEER, Richard, Perlee; 1115 Kelly Drive, Newark, DE 19711 (US). STAIB, Ronald, Richard; 12 Wordsworth Drive, Hyde Park, Wilmington, DE 19808 (US).		Published <i>With international search report.</i>
(74) Agent: ROSSI, Joanne, Mary, Fobare; Hercules Incorporated, Hercules Plaza, 1313 North Market Street, Wilmington, DE 19894-0001 (US).		
(54) Title: DIALDEHYDE-MODIFIED ANIONIC AND AMPHOTERIC POLYACRYLAMIDES FOR IMPROVING STRENGTH OF PAPER		
(57) Abstract		
Composition comprising crosslinked, thermosetting, water soluble polymer having nonionic moieties derived from acrylamide, methacrylamide or both; anionic moieties derived from α , β -unsaturated carboxylic acids having from 3 to 5 carbon atoms and salts thereof; and optionally cationic moieties derived from unsaturated monomers containing amino groups or quaternary ammonium groups, said polymer having aldehyde functionality.		

BEST AVAILABLE COPY

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

- 1 -

DIALDEHYDE-MODIFIED ANIONIC AND AMPHOTERIC POLYACRYLAMIDES FOR IMPROVING STRENGTH OF PAPER

Background of the Invention

Field of the Invention

This invention relates to improving the strength of paper and more particularly it relates to dialdehyde modified anionic and amphoteric polyacrylamides which when incorporated in paper result in improved strength.

5

Description of the Prior Art

Several anionic and amphoteric polyacrylamides have been, or are in the process of being, commercialized by Hercules Incorporated for the paper industry.

Anionic polyacrylamides comprised of acrylic acid with a small amount of crosslinker are described in US 5,543,446 the disclosure of which reference is hereby incorporated by reference. Amphoteric polyacrylamides comprised of methacryloyloxyethyl-trimethylammonium chloride (MTMAC) and itaconic acid with a small amount of crosslinker are described in WO 98/06898, the disclosure of which reference is hereby incorporated by reference. All of these materials improve the dry strength of paper via electrostatic attraction and hydrogen bonding.

15

Summary of the Invention

According to the present invention there is provided a composition comprising crosslinked thermosetting, water soluble polymer having nonionic moieties derived from acrylamide, methacrylamide or both; anionic moieties derived from α,β -unsaturated carboxylic acids having from 3 to 5 carbon atoms and salts thereof; moieties derived from water soluble divinyl monomer; and optionally cationic moieties derived from unsaturated monomers containing amino groups or

- 2 -

quaternary ammonium groups, said polymer having aldehyde functionality where the aldehyde functionality is derived from a dialdehyde. There is also provided a composition consisting essentially of crosslinked thermosetting, water soluble polymer having nonionic moieties derived from acrylamide, methacrylamide or 5 both; anionic moieties derived from α,β -unsaturated carboxylic acids having from 3 to 5 carbon atoms and salts thereof; and optionally cationic moieties derived from unsaturated monomers containing amino groups or quaternary ammonium groups, said polymer having aldehyde functionality where the aldehyde functionality is derived from a dialdehyde.

10 Further according to the present invention there are provided processes for preparing the polymer of the present invention; for making paper with such polymer; for making paper with such polymer in combination with a cationic adjunct; and paper comprising polymer of the present invention.

15 **Detailed Description of the Invention**

Surprisingly, it has been discovered that the reaction of dialdehydes (such as glyoxal) with anionic and amphoteric polyacrylamides results in improved dry strength and wet strength as well as providing repulpable or temporary wet strength.

20 The ionic prepolymers of the invention are made from nonionic monomer selected from the group consisting of acrylamide and methacrylamide, anionic monomer, and optionally cationic monomer. The amount of anionic monomer plus cationic monomer comprises from 1 to 50 mole percent of the total of anionic, 25 cationic, and nonionic monomer in the prepolymer. Acrylamide is the preferred nonionic monomer.

Anionic monomers are preferably α,β -unsaturated carboxylic acids having from 3 to 5 carbon atoms and salts thereof. Suitable anionic monomers are e.g., 30 acrylic acid, methacrylic acid, itaconic acid and salts hereof. Acrylic acid and itaconic acid are preferred. The preferable salts are sodium salts.

Cationic monomers can be unsaturated monomers containing amino groups or quaternary ammonium groups. When monomers containing amino groups are used, cationic sites are obtainable by forming salts of the amino groups with mineral acids. Preferred unsaturated cationic monomers are methacryloyloxyethyltrimethylammonium chloride (MTMAC), acryloyloxyethyltrimethylammonium chloride (ATMAC), diallyldimethylammonium chloride (DADMAC), methacrylamidopropyltrimethyl-ammonium chloride (MAPTAC), methacryloyloxyethylbenzyltrimethylammonium chloride (MBMAC), and the hydrochloride salt of dimethylaminoethylmethacrylate (DMAEMA-HCl). The most preferred cationic monomer is MTMAC.

The ionic prepolymers for use in the invention can have an amount of anionic monomer plus cationic monomer up to about 50 mole percent, preferably up to about 20 mole percent, and most preferably up to about 10 mole percent, of the total of anionic, cationic, and nonionic monomers. The mole percent anionic monomer plus cationic monomer can be at least about 1, preferably at least about 3, and most preferably at least about 5.

The amount of cationic monomer when present can be up to about to 25 mole percent, preferably up to about 10 mole percent, and most preferably up to about 5 mole percent. The amount of cationic monomer can be 0, preferably at least about 1 and most preferably at least about 2 mole percent.

The preferred molar ratio of cationic monomer to anionic monomer is at least about 1:10 and can be up to about 10:1, with the most preferred ratio being at least about 1:2 and can be up to about 2:1.

A small amount of water soluble divinyl monomer may also be incorporated to increase the molecular weight of the ionic prepolymer by crosslinking without rendering it insoluble. Suitable divinyl monomers are N,N'-methylenebisacrylamide,

- 4 -

ethyleneglycol dimethacrylate, and ethyleneglycol diacrylate. Preferably the divinyl monomer is N,N'-methylenebisacrylamide.

Preferred dialdehydes for reaction with the copolymer are glyoxal and C₃ to 5 about C₈ saturated or unsaturated dialdehydes. Examples of such dialdehydes include malonic dialdehyde, succinic dialdehyde, glutaraldehyde, adipic dialdehyde, 2-hydroxyadipic dialdehyde, pimelic dialdehyde, suberic dialdehyde, azelaic dialdehyde, sebacic dialdehyde, maleic aldehyde, fumaric aldehyde, phthalaldehyde, isophthalaldehyde, terephthalaldehyde, and 10 1,4-diformylcyclohexane. The most preferred dialdehyde is glyoxal.

The amount of dialdehyde used for reaction can be at least from about 0.01 moles for each mole of nonionic moiety (e.g., acrylamide) contained in the prepolymer, preferably at least about 0.1 moles, and most preferably at least from 15 0.2 moles for each mole of nonionic moiety in the prepolymer. The amount of dialdehyde can be up to about 1, preferably up to about 0.7 and most preferably up to about 0.5 moles for each mole of nonionic moiety in the prepolymer.

The polyacrylamide prepolymers are prepared by free-radical initiated 20 polymerization of acrylamide and an anionic monomer, such as acrylic acid, and optionally a cationic monomer, such as MTMAC. The product resin is prepared by reacting the prepolymer with dialdehyde, such as glyoxal to a target viscosity, followed by acid stabilization. The resulting product is a crosslinked, thermosetting, anionic or amphoteric resin containing aldehyde functionality.

25 The reaction between the dialdehyde and prepolymer can preferably be carried out at a pH of at least about 5 and it can be up to about 10 and a temperature of at least about 20°C and up to about 90°C for a time sufficient to reach the viscosity target for the product. More preferably the pH is at least about 30 8 and up to about 9 and the temperature is at least about 25 and up to about 50°C. During the reaction of dialdehyde with the prepolymer some crosslinking of the

product will occur through reaction of the aldehyde group with another amide-containing polymer chain. The crosslinking is accompanied by an increase in viscosity. The preferable target viscosity for the product is a Brookfield viscosity of at least about 50 cps as an 8.5% solids aqueous solution. The preferred target 5 viscosity can be up to about 500 cps. More preferably the target viscosity is at least about 100 and up to about 300 cps, and most preferably it is at least about 150 and up to about 250 cps.

By imparting cellulose reactive functionality to anionic or amphoteric 10 polyacrylamide compositions, better performance can be achieved. Cellulose reactivity can be imparted by derivitizing some of the acrylamide moieties e.g., with glyoxal. The reaction with glyoxal crosslinks or further crosslinks the resin backbone, which will often boost dry strength effectiveness, and also provides aldehyde functionality, which will react with cellulose hydroxyls. The reactions 15 between resin aldehydes and cellulose hydroxyls form reversible covalent bonds (hemiacetals) which boost dry strength performance and provide some reversible (temporary) wet strength.

The resins of the present invention can be added to paper pulp alone in the 20 case of amphoteric resins, or with a cationic adjunct to improve retention in the case of either the anionic or amphoteric versions. The resins of this invention also boost the performance of cationic wet strength or dry strength resins.

Examples of cationic adjuncts include polyaminopolyamide-epi resins (such 25 as Kymene® 557H wet-strength resin available from Hercules Incorporated), cationic starch, polyamines (such as Reten® 203 polyamine available from Hercules Incorporated), polyamine-epi resins (such as Reten® 204 resin available from Hercules Incorporated) and polyethyleneimine. Preferred cationic adjuncts are the polyaminopolyamide-epi resins and cationic starch. Most preferred cationic 30 adjuncts are the polyaminopolyamide-epi resins. When used alone, the dry strength effectiveness of the amphoteric resins of this invention is comparable to

- 6 -

that obtained with polyaminopolyamide-epi resins. When used in combination with polyaminopolyamide-epi resins, wet and dry strength performance is boosted by over 10% compared to the polyaminopolyamide alone. It is expected that paper treated with these resins alone would exhibit some wet strength (up to 50% of that obtained with polyaminopolyamide wet-strength resins at equal resin loading), and be more repulpable (on an equal strength basis) than paper treated with polyaminopolyamide-epi wet-strength resins.

By the term "cationic wet strength resin" is meant cationic polymers or adjuncts which when used alone in paper impart significant wet strength to the paper.

Polymeric amine/epihalohydrin resins are selected from the group consisting of polyaminoamide/epihalohydrin resins, polyalkylenepolyamine/epihalohydrin resins, aminopolymer/epihalohydrin resins, and polyaminoamide ureylene/epihalohydrin resins. The preferred epihalohydrin is epichlorohydrin..

The most preferred cationic wet strength resins for the practice of the invention are the polyaminoamide/epihalohydrin resins. Polyaminoamides containing tertiary amines in the backbone are disclosed in U.S. Patent Nos. 4,487,884 and 4,515,657 to Maslanka, both of which are incorporated herein by reference in their entireties. If tertiary amines are present in the polyaminoamide or polyamine backbone, quaternary epoxide groups are produced.

Kymene® wet strength resins are the preferred polyaminoamide/epihalohydrin resins. Some examples of polyaminoamide/epihalohydrin Kymene® wet strength resins, available from Hercules Incorporated, Wilmington, DE, are Kymene® 557H, Kymene® 557LX, Kymene® 557 SLX, Kymene® 557 ULX and Kymene® Plus. In Kymene® 557H adipic acid is reacted with diethylenetriamine to form a polyaminoamide that is alkylated and crosslinked with epichlorohydrin to form a polyaminoamide/epichlorohydrin resin. Kymene®Plus is a higher solids version of

- 7 -

Kymene® 557H, Kymene® 557LX, Kymene® 557SLX and Kymene® 557ULX are versions of Kymene® 557H that contain low amounts of halide by-products. Polyaminoamide/epichlorohydrin resins containing low amounts of halide by-products are disclosed in U.S. Patent No. 5,171,795, to Miller et al., which is
5 incorporated herein by reference in its entirety, European Patent Application Publication No. 0 488 767A2, to Bower, and European Patent Application Publication No. 0 510 987A1, to Bull et al.

Kymene® 450 wet strength resin is a polyaminoamide ureylene/epichlorohydrin resin prepared by reacting oxalic acid, methyl
10 bis(aminopropylamine) and urea to form a polyaminoamide ureylene, which is then alkylated with epichlorohydrin. Resins of this type are disclosed in U.S. Patent No. 4,487,884, to Maslanka.

Kymene® 736 is a polyalkylenepolyamine/epichlorohydrin resin prepared from hexamethylenediamine and epichlorohydrin as described in European Patent
15 Application Publication No. 0508203, October 14, 1992.

The level of cationic adjunct used will generally be in the range of from about 0.1% to about 5% on a dry basis based on the dry weight of pulp. A preferred level is from about 0.2% to about 4%, and a more preferred level from about 0.3% to about 3%. The most preferred level will be in the range of from about
20 0.3% to about 2%.

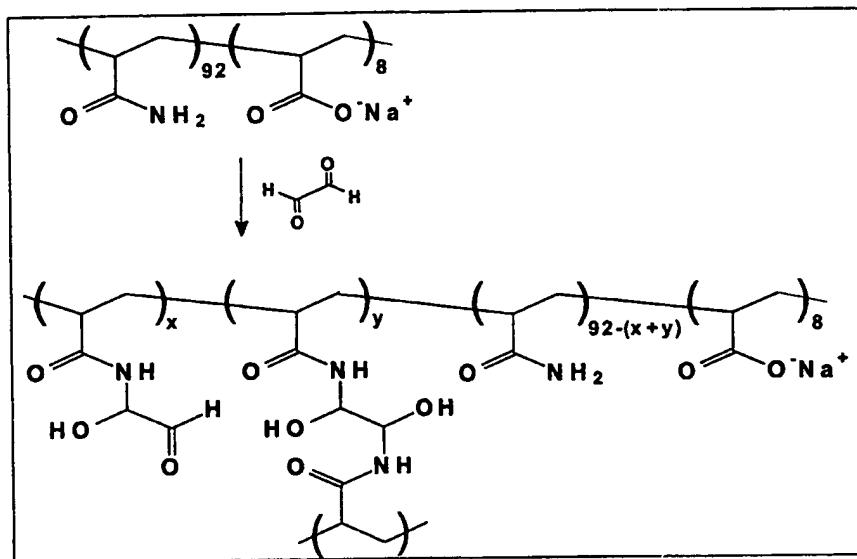
The synthetic scheme for a resin of the present invention based on an 8 mole percent acrylic acid anionic polyacrylamide is given in Figure 1. Examples of the synthesis of the anionic polyacrylamide prepolymer, including ranges of properties
25 and composition, are given in the above referred to US 5,543,466. Preferred prepolymer RSV is 0.5 to 2 dL/g. Preferred composition of acrylic acid is 4-12 mole percent. The prepolymer is diluted to 7 to 10% solids and glyoxal is added at ambient temperature. The mole ratio of glyoxal to acrylamide in the prepolymer ranges from 0.1 to 1.0. Preferred range is 0.15 to 0.5. Most preferred mole ratio is
30 0.25. The pH of the mixture is raised to about 9 with dilute NaOH. Solution viscosity (Gardner-Holdt) is monitored. After an increase of up to about 6 Gardner-

- 8 -

Holdt viscosity units, the reaction is quenched by reducing the reaction pH to about

3. Final solids range from 7 to 10%, with 8.5% preferred.

Figure 1



5

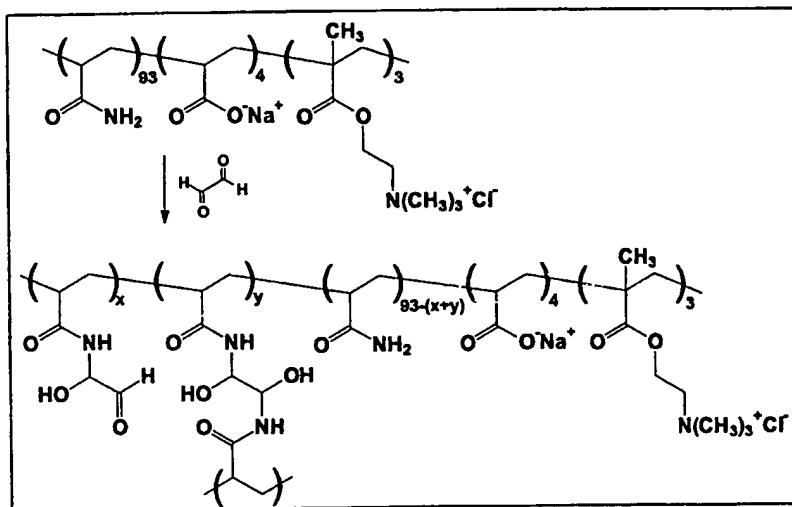
where X can be from 1 to 50, most preferably about 15. Y can be up to 5, most preferably about 1.

10 The synthetic scheme for a resin of the present invention based on a 4 mole percent acrylic acid/3 mole percent MTMAC amphoteric polyacrylamide is given in Figure 2.

15 Examples of the synthesis of the amphoteric polyacrylamide prepolymer are given in the above referred to WO 98/06898. Preferred prepolymer RSV is from 0.5 to 2 dL/g. MTMAC and acrylic acid content in the prepolymer are less than 10 mole percent. The reaction with glyoxal is the same as described for the anionic version above.

- 9 -

Figure 2



where X can be from 1 to 50, most preferably about 15. Y can be up to 5, most preferably about 1.

5

The product resins of the present invention are either anionic or amphoteric, crosslinked, thermosetting, and reactive with paper pulp fibers. For the anionic resins, a cationic adjunct or co-additive is usually necessary to retain the material on the anionic fiber surfaces. Such an adjunct can be a non-reactive material such as a retention aid (a polyDADMAC such as Reten® 203 retention aid or a cationic polyacrylamide such as Reten® 1232 retention aid) or a reactive resin (polyaminopolyamide-epi resin, such as Kymene® 557H, resin polyamine-epi resin such as Kymene® 736 resin, or glyoxalated cationic polyacrylamide such as Hercobond® 1366 resin). The amphoteric resins of this invention, due to the presence of the cationic quaternary ammonium groups, can be retained without the use of a cationic adjunct. Retention and performance, however, are usually increased by the use of a cationic adjunct.

When the amphoteric resins of this invention are used alone or when the anionic or amphoteric resins of this invention are used in combination with a non-reactive cationic retention aid, paper dry strength is improved. This dry strength

- 10 -

improvement is usually better than that obtained with conventional, uncrosslinked, unreactive dry strength resins. In addition, some wet strength is obtained. Because of the reversible nature of the hemiacetals that give rise to this wet strength, the wet strength is temporary, i.e., it decays rapidly over time. This
5 temporary nature makes paper treated with the resins of this invention more repulpable than conventional polyaminopolyamide-epi wet-strength resins, when compared on an equal wet strength basis.

When the cationic adjunct is a functional additive such as a
10 polyaminopolyamide-epi wet-strength resin, the resins of this invention significantly improve the wet and dry strength performance of the adjunct over non-dialdehyde-modified anionic or amphoteric polyacrylamides.

The scope of the present invention as claimed is not intended to be limited
15 by the following Examples which are given merely by way of illustration. All parts and percentages are by weight unless otherwise indicated.

Example 1

This examples describes the synthesis of a glyoxal-modified anionic
20 polyacrylamide with a low crosslink density.

An anionic polyacrylamide comprised of 8 mole percent of acrylic acid and 0.04 mole percent of methylenebisacrylamide with a 0.05% reduced specific viscosity (RSV) measured in 2 molal sodium chloride at 30°C in a Ubbelohde
25 viscometer of about 1.2 dL/g (500 g at 22.4% solids) and deionized water (1100 g) were charged at ambient temperature to a 3 neck 2-liter round bottom flask equipped with a mechanical stirrer, glass stirrer shaft with Teflon stir blade, and pH probe. Solids of the mixture was 7.0% by weight. The pH of the mixture was raised from 4.5 to 7.2 using dilute caustic. Glyoxal (51.98 g at 40% solids) was
30 added via syringe. The pH was raised to 8.5 with 10% NaOH. The Gardner-Holdt viscosity was measured immediately (ASTM method D803) and was found to be an

- 11 -

E+. The reaction pH was maintained at 8.5 while the Gardner-Holdt viscosity of the mixture was monitored. After 50 minutes, the viscosity was a G+. The reaction was quenched by lowering the pH to 4 with sulfuric acid. Total solids were 7.45%. The sample was stored under refrigeration.

5

Example 2

This example describes the synthesis of a glyoxal-modified anionic polyacrylamide with a high crosslink density.

10 The same anionic polyacrylamide prepolymer used to prepare the resin in Example 1 (500 g at 22.4 % solids) was charged to a flask equipped as described in Example 1. The polymer was diluted to 7% solids with deionized water (1100 g). The pH was adjusted to 7.45 with 10% NaOH. With stirring, glyoxal (51.95 g at 40% solids) was added to the flask an ambient temperature. 10% NaOH solution
15 was added to raise the pH of the mixture to 8.5. The Gardner-Holdt viscosity was E+. The pH was maintained at 8.5 while the viscosity was monitored. Once the viscosity increased 4-6 Gardner-Holdt units, the reaction was to be quenched. After 61 minutes, the viscosity had increased to J. The reaction was quenched by reducing the pH to 4.0 with sulfuric acid. Total solids were 7.88%. The mixture
20 was stored under refrigeration.

Example 3

25 This example describes the synthesis of a glyoxal-modified amphoteric polyacrylamide from a polyacrylamide prepolymer comprised of 4 mole percent of acrylic acid and 3 mole percent of MTMAC.

An amphoteric polyacrylamide comprised of 4 mole percent of acrylic acid and 3 mole percent of MTMAC having an RSV of 0.8 dL/g (131.0 g of a 17.5% solids solution, 22.9 g dry basis) was diluted to 7% solids with 196 g of water. The
30 solution pH was raised from 4.4 to 7 with 4.7 g of 5% caustic . Glyoxal (12.7 g of a 40% solution, 5.07 g dry basis) was added to the solution all at once, at ambient

- 12 -

temperature. The pH of the mixture was raised to 8.5 with 1.39 g of 5% caustic, again at ambient temperature. When the Gardner-Holdt viscosity (initially about "G") reached "M" (an increase of about 6 Gardner units in about 30 minutes), the crosslinking reaction was quenched by adding 2.5 g of 10% sulfuric acid to bring
5 the pH down to 3. Final solids were about 8.5%.

Example 4

10 This example describes the synthesis of a glyoxal-modified amphoteric polyacrylamide from a polyacrylamide prepolymer comprised of 2 mole of itaconic acid and 3 mole percent of MTMAC.

An amphoteric polyacrylamide comprised of 2 mole percent of itaconic acid and 3 mole percent of MTMAC having an RSV of 1.65 dL/g (60.0 g of a 16.4%
15 solids solution, 9.84 g dry basis) was diluted to 7% solids with 80.6 g of water. The solution pH was raised to 7 with 5% caustic . Glyoxal (18.6 g of a 40% solution, 7.42 g dry basis) was added to the solution all at once, at ambient temperature. The pH of the mixture was raised to 8.3 with 5% caustic, again at ambient
20 temperature. When the Gardner-Holdt viscosity (initially about "G") reached "I+" (an increase of about 2 Gardner units in about 10 minutes), the crosslinking reaction was quenched by adding 10% sulfuric acid to bring the pH down to 3. Final solids were about 9.9%.

Example 5 and 6 Comparative Examples 1 to 4

25

These examples describe an evaluation in paper, demonstrating the improvement in wet and dry strength performance of a polyaminopolyamide-epi wet-strength resin when used with resins of the invention.

30 Paper handsheets were prepared from a 50:50 hardwood:softwood bleached kraft dry lap pulp blend refined to about 500 mL Canadian standard freeness. Sheets were generated having 80 lb/3000 sq. ft. basis weight at a papermaking pH

of about 8. The tensile strengths were determined on two week naturally aged sheets by TAPPI methods T456 and T494. PAPAE = Kymene® 557H polyaminopolyamide-epi resin available from Hercules Incorporated. Pam = polyacrylamide. Ingredients and results are summarized in Table 1.

5

Table 1

Example	PAPAE (%)	Resin (%)	Dry Tensile (lbs/in)	Wet Tensile (lbs/in)
C-1	0	0	39.4	1.2
C-2	0.4	0	45.3	7.7
5	0.4	Example 1 (0.2)	47.2	8.1
6	0.4	Example 3 (0.2)	48.1	8.4
C-3	0.4	Anionic PAm ^(a) (0.2)	48.8	7.7
C-4	0.4	Amphoteric PAm ^(b) (0.2)	42.7	8.0

^(a)8 mole percent acrylic acid

^(b)4 mole percent acrylic acid, 3 mole percent MTMAC

10 These examples demonstrate that the resin of this invention boosted the wet and dry strength obtained by the PAPAE resin alone. The wet strength improvements obtained with the resins of the invention were better than that obtained with the polyacrylamides prior to the process of the invention.

15

Examples 7-9 and Comparative 5 and 6

These examples describe an evaluation in a groundwood newsprint furnish, demonstrating the improvement in dry strength provided by the resin formulation of Example 4.

20

Paper was prepared on a continuous papermaking former from a 95:5 blend of repulped groundwood newsprint (unrefined) and softwood bleached kraft pulp refined to about 410 mL Canadian standard freeness. Sheets were generated having 42 g/m² basis weight at a papermaking pH of about 4.5 with 1% alum. Control runs (no additives) were prepared at 42 and 45 g/m² basis weight for comparison. Ingredients and results are summarized in Table 2.

25

Table 2

Example	Basis Weight (g/m²)	Resin of Example 4 (%)	Dry Tensile (lbs/in)
C-5	42	0	8.4
C-6	45	0	9.5
7	42	0.2	9.6
8	42	0.4	9.9
9	42	0.8	10.3

- These examples demonstrate that the resin of this invention boosted dry strength of a 42 g/m sheet to a level even higher than that obtained with a heavier (45 g/m²) sheet without such resin. Higher levels of resin afforded higher strength.

Examples 10-13 and Comparative Examples 7 and 8

- These examples describe an evaluation in a recycled linerboard furnish, demonstrating the ability of the resins of this invention to impart both wet and dry strength when used alone, and to improve the wet and dry strength performance of a polyaminopolyamide-epi wet-strength resin.

Paper was prepared on a continuous papermaking former from repulped old corrugated containers (OCC) refined to about 400 mL Canadian standard freeness. Sheets were generated having 80 lb/3000 sq. ft. basis weight at a papermaking pH of about 6. All runs contained 1% alum and 0.75% cationic starch. PAPAE = low epi polyaminopolyamide-epi resin (epi:amine ratio = 0.25:1). Ingredients and results are summarized in Table 3.

- 15 -

Table 3

Example	PAPAE (%)	Resin (%)	Mullen Burst (psi)	Dry Tensile (lbs/in)	Ring Crush (lbs/in)	Wet Tensile (lbs/in)
C-7	0	0	59.5	36.4	45.6	1.7
10	0	Example 3 (0.5)	71.8	40.5	51.6	3.5
11	0	Example 4 (0.5)	60.4	38.6	48.7	2.5
C-8	0.5	0	71.8	39.5	52.4	3.2
12	0.5	Example 3 (0.5)	73.0	42.6	57.3	4.9
13	0.4	Example 4 (0.5)	73.1	42.6	52.5	4.2

5

Example 14 and Comparative Examples 9 and 10

These examples describe an evaluation in a liquid packaging board furnish, demonstrating the ability of a resin of this invention to improve the wet and dry strength performance of a polyaminopolyamide-epi wet-strength resin.

10

Paper was prepared on a continuous papermaking former from a 70:30 hardwood:softwood bleached kraft pulp blend refined to about 500 mL Canadian standard freeness. Sheets were generated having 180 lb/3000 sq. ft. basis weight at a papermaking pH of about 8. The strength data were determined on two week naturally aged sheets. All runs contained 0.5% cationic starch and 0.2% AKD size. PAPAE = Kymene® 557H polyaminopolyamide-epi resin. Ingredients and results are summarized in Table 4.

- 16 -

Table 4

Example	PAPAE (%)	Resin (%)	ZDT ⁽¹⁾ (psi)	Mullen Burst (psi)	Dry Tensile (lbs/in)	Wet Tensile (lbs/in)
C-9	0	0	60.3	101	69.6	2.9
C-10	0.5	0	74.8	133	84.2	18.0
14	0.5	Example 4 (0.5)	95.5	155	93.9	19.9

⁽¹⁾Z direction tensile strength determined by TAPPI method T541.

5

Example 15

This example describes the synthesis of a glyoxal-modified acrylamide/methacrylic acid copolymer.

10

Dilute five hundred grams of a 20% solution of a 10 mole percent methacrylic acid/90 mole percent acrylamide copolymer to 7% solids with 928.6 grams of deionized water in the reactor. Adjust the pH to 7.5 with 10% NaOH. With stirring, add glyoxal (45.0 grams of 40% solution) to the flask at ambient temperature, and add 10% NaOH solution to raise the pH to 8.5. Maintain pH at 8.5 while monitoring the viscosity. The initial Gardner-Holdt viscosity of E increases to J over a period of one hour. Quench the reaction by reducing the pH to 4.0 with sulfuric acid giving a final solids of 7.8%. Store the product under refrigeration.

15
20

Example 16

This example describes the synthesis of a glyoxal-modified amphoteric copolymer of DADMAC, acrylic acid, and acrylamide.

25

Dilute six hundred twenty-five grams of a 16.0% solution of a 5 mole percent acrylic acid/5 mole percent DADMAC/90 mole percent acrylamide copolymer to 7% solids with 803.6 grams of deionized water in the reactor. Adjust the pH to 7.5 with 10% NaOH. With stirring, add glyoxal (43.2 grams of 40% solution) to the flask at ambient temperature, and add 10% NaOH solution to raise the pH to 8.5. Maintain

- 17 -

the pH at 8.5 while monitoring the viscosity. The initial Gardner-Holdt viscosity of D increases to I over a period of 80 minutes. Quench the reaction by reducing the pH to 4.0 with sulfuric acid giving a final solids of 7.5%. Store the product under refrigeration.

5

Examples 17-19 and Comparative Examples 11-13

This example describes an evaluation in a liquid packaging board furnish, demonstrating the ability of a resin of this invention to improve the dry strength performance of an polyaminopolyamide-epi wet-strength resin with or without added cationic starch.

10

Paper was prepared on a continuous papermaking former from a 70:30 hardwood:softwood bleached kraft pulp blend refined to about 500 mL Canadian standard freeness. Sheets were generated having 180 lb/3000 sq. ft. basis weight 15 at a papermaking pH of about 8. The strength data were determined on two week naturally aged sheets. All runs contained 0.2% AKD size. PAPAE = Kymene® 557H polyaminopolyamide-epi resin.

Example	Cationic Starch %	PAPAE %	Resin %	ZDT (psi)
C-11	0	0.3	0	55.2
17	0	0.3	Example 2 (0.3)	66.2
C-12	0.5	0.5	0	61.2
18	0.5	0.5	Example 2 (0.3)	91.1
C-13	1.0	0.3	0	67.7
19	1.0	0.3	Example 2 (0.3)	84.4

Claims

1. A composition comprising crosslinked thermosetting, water soluble polymer having nonionic moieties derived from acrylamide, methacrylamide or both; anionic moieties derived from α,β -unsaturated carboxylic acids having from 3 to 5 carbon atoms and salts thereof; moieties derived from water soluble divinyl monomer and optionally cationic moieties derived from unsaturated monomers containing amino groups or quaternary ammonium groups, said polymer having aldehyde functionality wherein the aldehyde functionality is derived from a dialdehyde.
2. A composition consisting essentially of crosslinked thermosetting, water soluble polymer having nonionic moieties derived from acrylamide, methacrylamide or both; anionic moieties derived from α,β -unsaturated carboxylic acids having from 3 to 5 carbon atoms and salts thereof; and optionally cationic moieties derived from unsaturated monomers containing amino groups or quaternary ammonium groups, said polymer having aldehyde functionality wherein the aldehyde functionality is derived from a dialdehyde.
3. The composition of claims 1-2 wherein the combined amount of anionic and cationic moieties in the polymer is at least about 1 mole % based on the total amount of anionic, cationic and nonionic monomers.
4. The composition of claim 3 wherein the combined amount of anionic and cationic moieties in the polymer is at least about 3 mole %.
5. The composition of claim 3 wherein the combined amount of anionic and cationic moieties in the polymer is at least about 5 mole %.

- 19 -

6. The composition of claims 1-5 wherein the combined amount of anionic and cationic moieties in the polymer is up to about 50 mole % based on the total amount of anionic, cationic and nonionic moieties.

5 7. The composition of claim 6 wherein the combined amount of anionic and cationic moieties in the polymer is up to about 20 mole %.

8. The composition of claim 6 wherein the combined amount of anionic and cationic moieties in the polymer is up to about 10 mole %.

10 9. The composition of claims 1-8 wherein the amount of cationic moieties is at least about 1 mole %.

15 10. The composition of claim 9 wherein the amount of cationic moieties is at least about 2 mole %.

11. The composition of claims 1-10 wherein the amount of cationic moieties is up to about 25 mole %.

20 12. The composition of claim 11 wherein the amount of cationic moieties is up to about 10 mole %.

13. The composition of claim 11 wherein the amount of cationic moieties is up to about 5 mole %.

25 14. The composition of claims 1-9 wherein the amount of cationic moieties is 0 mole %.

15. The composition of claims 1-4 wherein the molar ratio of cationic
30 moieties to anionic moieties is at least about 1:10.

- 20 -

16. The composition of claim 15 wherein the molar ratio of cationic moieties to anionic moieties is at least about 1:2.

17. The composition of claims 1-16 wherein the molar ratio of cationic 5 moieties to anionic moieties is up to about 10:1.

18. The composition of claim 17 wherein the molar ratio of cationic moieties to anionic moieties is up to about 2:1.

10 19. The composition of claims 1-18 additionally comprising moieties derived from water soluble divinyl monomer.

20. The composition of claims 1-19 wherein the moieties derived from 15 divinyl monomer are selected from the group consisting of N,N'-methylenebisacrylamide, ethyleneglycol dimethacrylate, and ethyleneglycol diacrylate.

21. The composition of claim 20 when the water soluble is divinyl monomer N,N'-methylenebisacrylamide.

20 22. The composition of claims 1-21 wherein the amount of aldehyde functionality is at least about 0.01 mole per mole of nonionic moiety.

25 23. The composition of claim 22 wherein the aldehyde functionality is at least about 0.1 mole per mole of nonionic moiety.

24. The composition of claim 22 wherein the aldehyde functionality is at least about 0.2 mole per mole of nonionic moiety.

30 25. The composition of claims 1-24 wherein the amount of aldehyde functionality is up to about 1 mole per mole of nonionic moiety.

26. The composition of claim 25 wherein the aldehyde functionality is up to about 0.5 mole per mole of nonionic moiety.

5 27. The composition of claim 25 wherein the aldehyde functionality is up to about 0.7 mole per mole of nonionic moiety.

28. The composition of claims 1-26 wherein the Brookfield viscosity of the polymer is at least about 50 cps as a 8.5% by weight aqueous solution.

10 29. The composition of claim 28 wherein the Brookfield viscosity of the polymer is at least about 100 cps.

15 30. The composition of claim 29 wherein the Brookfield viscosity of the polymer is at least about 150 cps.

31. The composition of claims 1-30 wherein the Brookfield viscosity of the polymer is up to about 500 cps as a 8.5% by weight aqueous solution.

20 32. The composition of claim 31 wherein the Brookfield viscosity of the polymer is up to about 300 cps.

33. The composition of claim 31 wherein the Brookfield viscosity of the polymer is up to about 250 cps.

25 34. The composition of claims 1-33 wherein the aldehyde functionality is derived from dialdehydes selected from the group consisting of glyoxal, saturated dialdehydes having from 3 to 8 carbon atoms and unsaturated dialdehydes having from 3 to 8 carbon atoms.

- 22 -

35. The composition of claim 34 wherein the aldehyde functionality is derived from dialdehydes selected from the group consisting of glyoxal, malonic dialdehyde, succinic dialdehyde, glutaraldehyde, adipic dialdehyde, 2-hydroxyadipic dialdehyde, pimelic dialdehyde, suberic dialdehyde, azelaic dialdehyde, sebacic dialdehyde, maleic aldehyde, fumaric aldehyde, phthalaldehyde, isophthalaldehyde, terephthalaldehyde, and 1,4-diformylcyclohexane.

36. The composition of claim 34 wherein the aldehyde functionality is derived from glyoxal.

37. The composition of claims 1-36 wherein the anionic moieties are derived from acrylic acid, methacrylic acid, itaconic acid and salts thereof.

38. The composition of claims 1-37 wherein the cationic moieties are derived from monomers selected from the group consisting of methacryloyloxyethyltri-methylammonium chloride, acryloyloxyethyltrimethylammonium chloride, diallyldimethylammonium chloride, methacrylamidopropyltrimethylammonium chloride, 20 methacryloyloxyethylbenzyldimethylammonium chloride and the hydrochloride salt of dimethylaminoethylmethacrylate.

39. The composition of claim 38 wherein the cationic moieties are derived from methacryloyloxyethyltrimethylammonium chloride.

40. A process for preparing the polymer of claims 1-39 comprising:
(a) providing a prepolymer comprising nonionic moieties derived from acrylamide, methacrylamide or both; anionic moieties derived from α,β -unsaturated carboxylic acids having from 3 to 5 carbon atoms and salts thereof; and optionally cationic moieties derived from unsaturated monomers containing amino groups or 30 quaternary ammonium groups and

- 23 -

(b) contacting said prepolymer with dialdehyde selected from the group consisting of glyoxal, saturated dialdehydes having from 3 to 8 carbon atoms and unsaturated dialdehydes having from 3 to 8 carbon atoms resulting in crosslinked, thermosetting resin containing aldehyde functionality.

5

41. The process of claim 40 wherein the prepolymer is contacted with the dialdehyde at a pH of at least about 5.

10 42. The process of claim 41 wherein the prepolymer is contacted with the dialdehyde at a pH of at least about 8.

43. The process of claims 40-42 wherein the prepolymer is contacted with the dialdehyde at a pH of up to about 10.

15 44. The process of claim 43 wherein the prepolymer is contacted with the dialdehyde at a pH of up to about 9.

45. The process of claims 40-44 wherein the prepolymer is contacted with the dialdehyde at a temperature of at least about 20°C.

20 46. The process of claim 45 wherein the prepolymer is contacted with the dialdehyde at a temperature of at least about 25°C.

25 47. The process of claims 40-46 wherein the prepolymer is contacted with the dialdehyde at a temperature of up to about 90°C.

48. The process of claim 47 wherein the prepolymer is contacted with the dialdehyde at a temperature of up to about 50°C.

30 49. The process of claims 40-48 wherein the prepolymer is contacted with the dialdehyde until the resulting resin has a Brookfield viscosity of at least about

- 24 -

50 cps as a 8.5% by weight aqueous solution.

50. The process of claim 49 wherein the prepolymer is contacted with the dialdehyde until the resulting resin has a Brookfield viscosity of up to about 500
5 cps.

51. The process of claim 50 wherein the prepolymer is contacted with the dialdehyde until the resulting resin has a Brookfield viscosity of up to about 300
cps.

10 52. The process of claim 51 wherein the prepolymer is contacted with
dialdehyde until the resulting resin has a Brookfield viscosity of up to about 250
cps.

15 53. The process of claims 49-52 wherein the prepolymer is contacted with
the dialdehyde until the resulting resin has a Brookfield viscosity of at least about
100 cps.

20 54. The process of claim 53 wherein the prepolymer is contacted with
dialdehyde until the resulting resin has a Brookfield viscosity of at least about 150
cps.

25 55. The process of claims 40-54 wherein the prepolymer is contacted with
the dialdehyde until the resulting resin has a Brookfield viscosity of from about 150
to about 250 cps, and wherein the amount of dialdehyde is from about 0.2 to about
0.5 mole per mole of nonionic moiety in the prepolymer.

56. The process of claims 40-55 wherein the prepolymer additionally
comprises moieties derived from water soluble divinyl monomer.

- 25 -

57. The process of claims 40-55 wherein the prepolymer additionally comprises moieties derived from water soluble divinyl monomer selected from the group consisting of N,N'-methylenebisacrylamide, ethyleneglycol dimethacrylate, and ethyleneglycol diacrylate.

5

58. The process of claim 57 wherein water soluble divinyl monomer is N,N'-methylenebisacrylamide.

59. A process for making paper having improved dry strength and wet
10 strength comprising:
(a) providing an aqueous suspension of pulp fibers;
(b) adding to the aqueous suspension at least one crosslinked thermosetting, water
soluble polymer according to any of claims 1-39; and
(c) sheeting and drying the aqueous suspension to obtain paper having better dry
15 strength and wet strength than paper that is substantially the same except that it
does not contain said crosslinked, thermosetting polymer.

60. A process for making paper having improved strength comprising:
(a) providing an aqueous suspension of pulp fibers;
20 (b) adding to the aqueous suspension (i) at least one crosslinked, thermosetting
polymer according to any of claims 1-39 and (ii) at least one cationic adjunct resin;
and
(c) sheeting and drying the aqueous suspension to obtain paper having better dry
strength and wet strength than paper that is substantially the same except that it
25 does not contain said crosslinked, thermosetting polymer.

61. The process of claim 60 wherein the cationic adjunct resin is selected
from the group consisting of polyaminopolyamide epichlorohydrin resin, cationic
starch, polyamines, polyamine epichlorohydrin resins and polyethyleneimine.

30

- 26 -

62. The process of claims 60-61 wherein wherein the cationic adjunct resin is polyaminopolyamide epichlorohydrin resin.

63. Paper comprising at least one crosslinked thermosetting, water soluble 5 polymer according to any of claims 1-39.

64. Paper comprising:

- (a) at least one crosslinked, thermosetting, water soluble polymer according to any of claims 1 -39 and
- 10 (b) at least one cationic adjunct resin.

INTERNATIONAL SEARCH REPORT

Interr. Application No
PCT/US 99/18706

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F8/28 D21H17/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 98 06898 A (HERCULES INCORPORATED) 19 February 1998 (1998-02-19) cited in the application page 6, line 7 -page 9, line 8; claims 1-33 ---	1-64
Y	EP 0 678 528 A (CASSELLA AG) 25 October 1995 (1995-10-25) page 3, line 1 - line 42 page 4, line 31 -page 5, line 7 page 5, line 46 -page 6, line 10; claims 1-10 ---	1-64
Y	WO 93 02115 A (NATIONAL DIAGNOSTICS) 4 February 1993 (1993-02-04) page 11, line 1 -page 12, line 22 page 17, line 11 -page 18, line 18; claims 1-67 ---	1-64
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority, claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

1 December 1999

16/12/1999

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Permentier, W

INTERNATIONAL SEARCH REPORT

Interr. ial Application No

PCT/US 99/18706

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>DATABASE WPI Section Ch, Week 8312 Derwent Publications Ltd., London, GB; Class A14, AN 1983-28504K XP002124444 & JP 58 023994 A (SHOWA DENKO KK), 12 February 1983 (1983-02-12) abstract ---</p>	1-64
A	<p>DATABASE WPI Section Ch, Week 8048 Derwent Publications Ltd., London, GB; Class A97, AN 1980-85192C XP002124445 & JP 55 132800 A (MITSUBISHI CHEM IND LTD) , 15 October 1980 (1980-10-15) abstract ---</p>	1
A	<p>US 4 135 969 A (D. R. COSPER) 23 January 1979 (1979-01-23) the whole document ---</p>	1
A	<p>US 4 199 643 A (D. R. FALGIATORE) 22 April 1980 (1980-04-22) column 3, line 66 -column 5, line 38; claims 1-21 ---</p>	1
A	<p>US 5 401 810 A (R. H. JANSMA) 28 March 1995 (1995-03-28) claims 1-13 ---</p>	1
A	<p>US 4 954 538 A (D. L. DAUPLAISE) 4 September 1990 (1990-09-04) claims 1-9 -----</p>	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Interr. Application No
PCT/US 99/18706

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
WO 9806898	A	19-02-1998	AU	3913197 A		06-03-1998
EP 678528	A	25-10-1995	DE FI	4414267 A 951859 A		26-10-1995 24-10-1995
WO 9302115	A	04-02-1993	AT AU AU AU CA DE EP EP JP	164381 T 687724 B 2427892 A 5108798 A 2113178 A 69224907 D 0594790 A 0808853 A 7500126 T		15-04-1998 05-03-1998 23-02-1993 19-03-1998 04-02-1993 30-04-1998 04-05-1994 26-11-1997 05-01-1995
JP 58023994	A	12-02-1983		NONE		
JP 55132800	A	15-10-1980		NONE		
US 4135969	A	23-01-1979		NONE		
US 4199643	A	22-04-1980	US	4279959 A		21-07-1981
US 5401810	A	28-03-1995	US	5490904 A		13-02-1996
US 4954538	A	04-09-1990	US US	5041503 A 5320711 A		20-08-1991 14-06-1994

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:



BLACK BORDERS



IMAGE CUT OFF AT TOP, BOTTOM OR SIDES



FADED TEXT OR DRAWING



BLURRED OR ILLEGIBLE TEXT OR DRAWING



SKEWED/SLANTED IMAGES



COLOR OR BLACK AND WHITE PHOTOGRAPHS



GRAY SCALE DOCUMENTS



LINES OR MARKS ON ORIGINAL DOCUMENT



REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY



OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.